Available online at www.sciencedirect.com
SCIENCE DIRECT®
Geochimica et Cosmochimica Acta 70 (2006) 2063–2072
Geochimica
www.elsevier.com/locate/gca

Different response of δD values of *n*-alkanes, isoprenoids, and kerogen during thermal maturation

Nikolai Pedentchouk *, Katherine H. Freeman, Nicholas B. Harris [1]

Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, USA

Received 28 March 2005; accepted in revised form 18 January 2006

Abstract

This study investigates the extent of post-depositional alteration of δD values of *n*-alkyl lipids, isoprenoids, and kerogen isolated from a continuous 450 m core that covers the transition from thermally immature to early mature sediments in the lacustrine Kissenda Formation, Lower Cretaceous, Gabon Basin. Large variations in δD values (up to 40‰ for nC_{17} and up to 30‰ for nC_{29} alkanes as well as up to 10‰ for kerogen) in closely spaced samples are evident throughout the core and remain preserved even at the bottom of the section. δD values of individual *n*-alkanes show a slight overall D-enrichment with depth, and a general trend of increasing δD values with increasing *n*-alkane chain length characterizes all samples, particularly in those below 600 m depth. Hydrogen isotopic compositions of kerogen samples overlap with those of *n*-alkanes throughout the section. δD values of pristane and phytane are more negative than those of nC_{17} alkane by as much as 120‰ at shallow depths but increase dramatically and approach δD values of nC_{17} alkane in the samples closest to the oil window. Integration of analytical and computational results indicates that: (1) *n*-alkanes and isoprenoids have the potential to preserve the original biological signal before the onset of oil generation; (2) isomeric and structural rearrangements taking place at the beginning stages of oil generation do not influence significantly the δD values of *n*-alkanes and kerogen. However, these processes have a major effect on the isotopic composition of isoprenoids, causing isotopic D-enrichment up to 90‰.

1. Introduction

Recent advances in hydrogen isotope analyses (Burgoyne and Hayes, 1998; Hilkert et al., 1999) open new opportunities for using δD values of lipids as a hydrological proxy for paleoenvironmental research. For example, variations in δD values of individual compounds record changes in paleohydrology during the Late Miocene (Andersen et al., 2001), the Late Quaternary (Huang et al., 2002; Liu and Huang, 2005; Schefuß et al., 2005), and the Holocene (Xie et al., 2000). Application of this proxy to older sediments was explored by Radke and Gleixner (2003), who used δD values of *n*-alkanes to reconstruct paleoclimatic and paleoenvironmental conditions during the Permo-Carboniferous. Li et al. (2001) recognized different sources (marine vs. lacustrine) of environmental water during the deposition of Paleozoic and Mesozoic rocks based on δD values of oil-derived *n*-alkanes. However, improved interpretations and future applications of organic hydrogen isotope data demand insights to the key factors that influence δD values of sedimentary organic matter (OM). These factors include: (1) complexities in the composition of paleoenvironmental waters, (2) D/H composition of biological precursor compounds, and (3) post-depositional processes that exchange hydrogen between OM and formation waters.

Normal alkanes and isoprenoids (specifically pristane and phytane) provide an attractive target for exploring the fate of sedimentary OM hydrogen because of their wide

* Corresponding author. Present address: Department of Geology and Geophysics, Yale University, P.O. Box 208109, New Haven, CT 06520, USA. Fax: +1 203 432 3134.
E-mail address: nikolai.pedentchouk@yale.edu (N. Pedentchouk).
[1] Present address: Department of Geology and Geological Engineering, Colorado School of Mines, 1516 Illinois Street, Golden, CO 80401, USA.

0016-7037/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.gca.2006.01.013

distribution in sedimentary samples and well-constrained OM precursor-sedimentary compound relationships. Modern laboratory and field studies of aquatic and terrestrial plants and lacustrine sediments show that *n*-alkyl lipid δD values generally fall between $\sim -150‰$ and $-250‰$, with an isotopic depletion relative to environmental water by $\sim 100‰$ to $200‰$ (Sessions et al., 1999; Sauer et al., 2001; Chikaraishi and Naraoka, 2003, 2005; Yang and Huang, 2003; Sachse et al., 2004; Smith and Freeman, in press). However, phytol (the most likely precursor for sedimentary pristane and phytane) is significantly more D-depleted, with δD values being typically more negative than $-300‰$ (Sessions et al., 1999; Chikaraishi et al., 2004, 2005; Chikaraishi and Naraoka, 2005), indicating very large isotopic fractionation relative to growth water.

Preservation of large differences between δD values of *n*-alkanes and isoprenoids (i.e., pristane and phytane) in thermally immature Late Carboniferous to Late Permian torbanites were reported by Dawson et al. (2004). Both pristane and phytane are D-depleted by ca. 60–80‰ relative to *n*-alkanes. Another study by Dawson et al. (2005) reported isotopic composition of *n*-alkanes and isoprenoids in Lower Triassic thermally immature to late mature sediments and oils. The difference in δD values of pristine and phytane vs. *n*-alkanes progressively decreases from ca. 115‰ in immature to ca. 0–19‰ in late mature sediments. δD values of pristane/phytane in oils show a slight overall D-enrichment of isoprenoids by ca. 13–14‰. An absence of significant hydrogen isotopic differences between *n*-alkanes and pristane/phytane in oils was also reported by Li et al. (2001), Schimmelmann et al. (2004), and Sessions et al. (2004). This similarity of δD values between *n*-alkanes and isoprenoids in late mature sediments and oils indicates a significant alteration of biological δD signature. The interpretation that isoprenoids become more D-enriched faster than *n*-alkanes with increasing maturity is tied to the branched nature of these compounds (Dawson et al., 2005). Branched structures undergo faster D-enrichment because of the presence of tertiary carbon carbocation centers, which promote extensive hydrogen exchange at the adjacent carbons (Alexander et al., 1984).

The above studies are based on either isolated snapshots of OM maturation process, e.g., thermally immature torbanites (Dawson et al., 2004) and oils (Li et al., 2001; Schimmelmann et al., 2004; Sessions et al., 2004) or a limited number of samples (2–3 per maturity level) from four different wells (Dawson et al., 2005). Here, we test the influence of thermal maturity on molecular deuterium signatures with a new continuous record of δD values of *n*-alkanes, pristane/phytane, and kerogen through the transition from thermally immature to early mature Lower Cretaceous ($\sim$120 to 140 Ma) lacustrine sediments in West Africa. Lacustrine systems are highly sensitive to paleohydrological and paleoclimatic changes and isotopic signals preserved in lacustrine derived OM are more variable than that from marine systems. Hence the wide range in deuterium signatures in OM from lacustrine settings provides an ideal opportunity for investigating post-depositional alteration of biological δD signal during thermal maturation. We attempt to advance our understanding of post-depositional alteration of indigenous δD signatures by integrating our empirical observations with theoretically determined isotopic parameters.

2. Methodology

2.1. Sample description and preparation

A total of 27 core samples of shale from the well ONEZ-1 representing a 450-m thick section ($\sim$7 Ma years) of lacustrine sediments from the Kissenda Formation (Neocomian) (Fig. 1) were used in this study for bulk OM and biomarker analyses. The Kissenda Formation, which extends from 415 to 908 m depth in this well, abruptly but conformably overlies medium to coarse grained sandstones of the Grès de Base, the basal unit of the rift sequence and is unconformably overlain by sandstones, siltstones and shales of the Aptian Gamba Formation. In this well, the Kissenda consists largely of shale, with approximately 1.5% sandstone and a similar proportion of limestone and dolomite, which occur as interbeds from 10 to 120 cm thick within the shale.

Total organic carbon (TOC) ranges between 0.9 and 7.9 wt.% (Fig. 2). Hydrogen Index (HI) values vary between 219 and 839, the majority are >500. Oxygen Index (OI) values range between 7 and 65, most of the values being <40. Based on HI and OI, kerogen type from the majority of the samples can be characterized as predominately Type I. However, elevated OI values in samples from 495 to 869.2 m depth indicate that these two samples contain Type I kerogen with a significant proportion of Type III kerogen. Predominance of short- and mid-chain *n*-alkanes in the saturate fraction (Fig. 3) also indicates a high proportion of algal-derived OM in these samples.

The total bitumen fraction was obtained by extracting ground samples for 24 h in a Soxhlet apparatus with dichloromethane. The saturate fraction was eluted using hexane, the aromatic fraction by hexane/dichloromethane (1:1 v/v), and the resin fraction by methanol, respectively. Normal alkanes were separated from isoalkanes and cycloalkanes using urea adduction, following the procedure described by Wakeham and Pease (1992).

2.2. Gas chromatography/mass spectrometry of biomarkers

Identification of compounds were made using an Agilent Technologies 6890 gas chromatograph interfaced with a HP 5973 mass spectrometer with hydrogen as the carrier gas. Hopane and sterane biomarker parameters from the saturate fraction were determined on GC/MS data and interpreted according to Peters and Moldowan (1993). The following ratios were calculated using peak areas on m/z 191 and 217 chromatograms: $Ts/(Ts + Tm)$, Ts/C_{30} hopane, $22S/(22S + 22R)$ C_{31} homohopanes, $20S/(20S +$

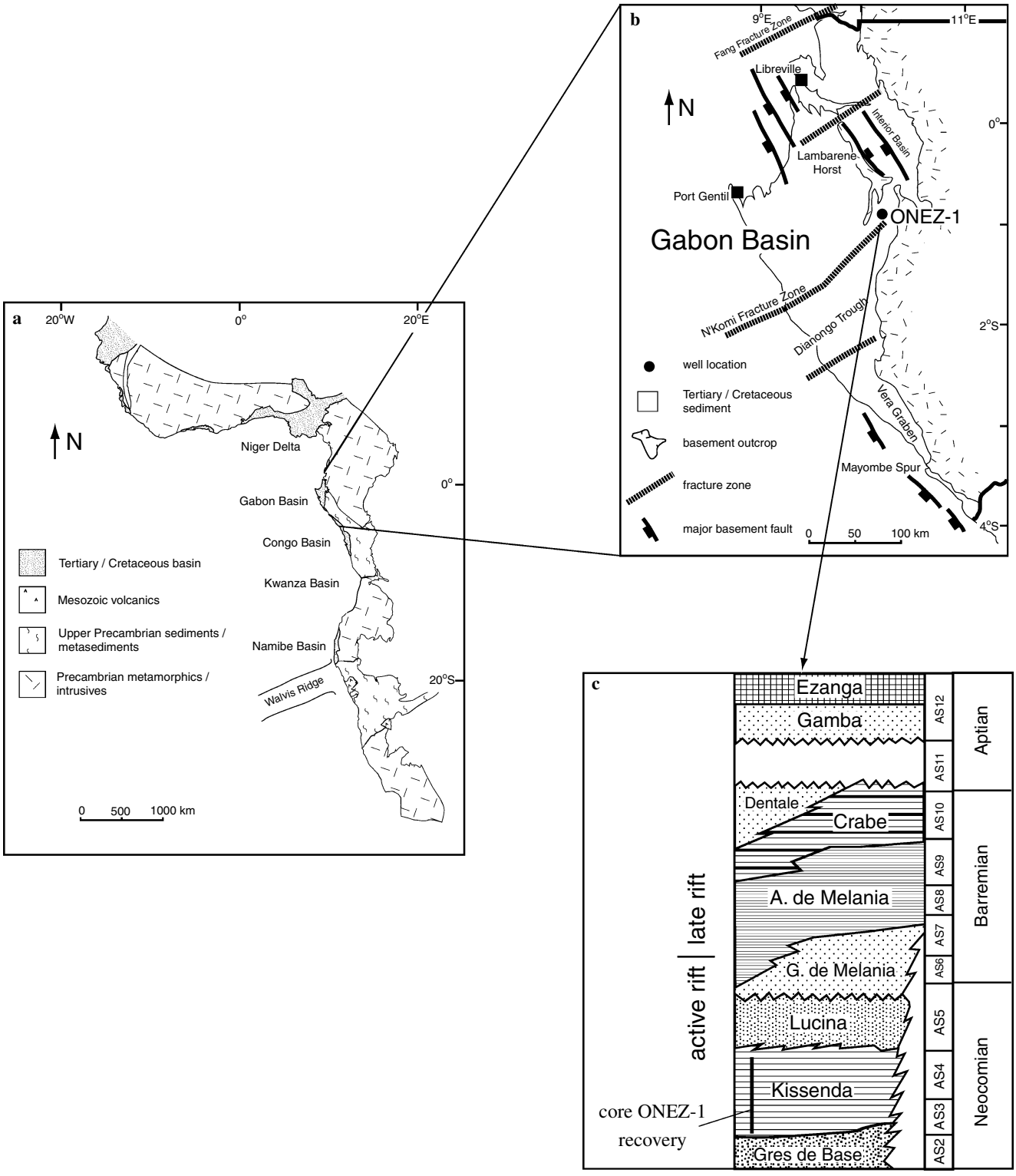

Fig. 1. (a) Location of the Gabon Basin on the equatorial West African margin, simplified from Davison (1999). (b) Gabon map showing well ONEZ-1, simplified from Teisserenc and Villemin (1990). (c) Stratigraphy of the Gabon Basin.

20*R*) C_{29} steranes, and Dia/Regular C_{27} steranes. Carbon preference index (CPI) values were determined on *n*-alkanes from the saturate fraction using integrated peak areas on *m*/*z* 57 chromatograms following Bray and Evans (1961).

2.3. Kerogen isolation and δD analyses

Kerogens were prepared from 20 samples following a modified HF-BF_3 method introduced by Robl and Davis (1993). Soxhlet-extracted powdered rock samples were first

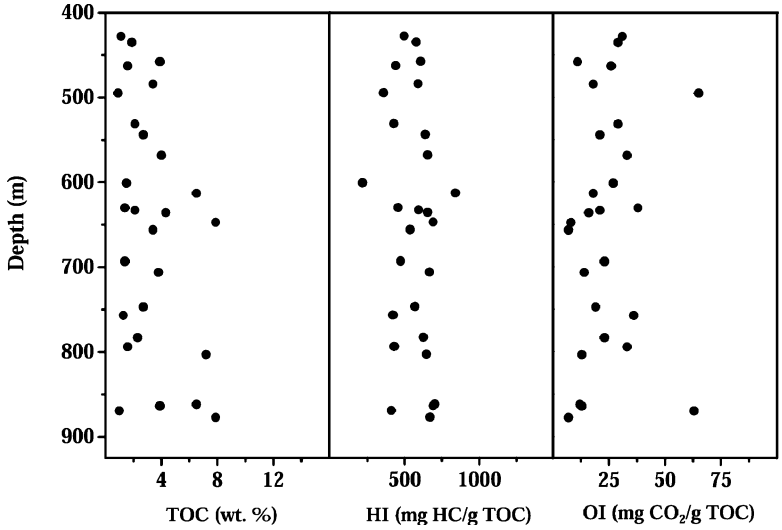

Fig. 2. Bulk organic matter parameters: Total Organic Carbon (TOC), Hydrogen Index (HI), and Oxygen Index (OI).

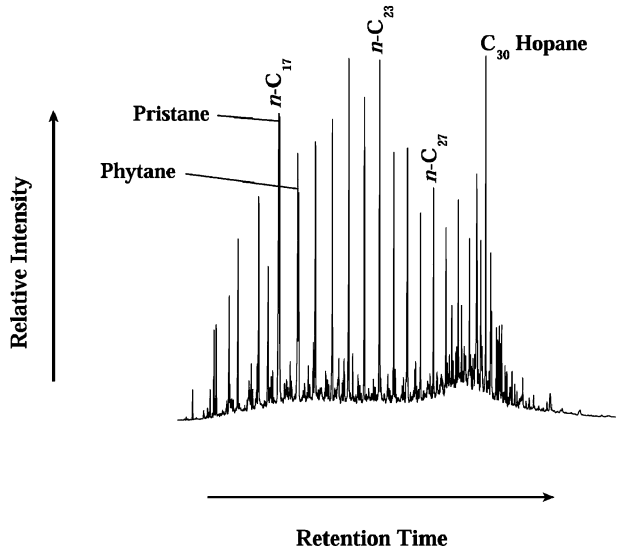

Fig. 3. Representative chromatogram of the saturate fraction, sample 656 m. All samples investigated in this are characterized by significant contribution from short-, mid-, and long-chain *n*-alkanes as well as pristane and phytane in the saturate fraction.

treated by 0.5 N HCl. The remaining portion was subjected to HF and then to H_3BO_3. Heavy minerals remaining after HF treatment were isolated from kerogen using $ZnBr_2$ heavy liquid separation. Kerogen was washed with distilled water and freeze-dried. Following hydrogen isotopic analyses (see below), five randomly chosen samples were re-extracted with dichloromethane and reanalyzed for their H isotopic composition. δD values of kerogen measured before and after the second solvent extraction differed by less than 2‰. Hence we assume that the initial soxhlet extraction removed the major portion of soluble OM. Hydrogen isotopic compositions of kerogen samples were determined using a ThermoFinnigan Delta-Plus XP mass spectrometer connected to a ThermoFinnigan TC/EA. Pyrolytic conversion of organic hydrogen to H_2 was conducted at 1450 °C followed by separation of gas products by a GC operating at 70 °C. The H_3-factor was determined daily using H_2 reference gas. Precision of isotopic measurement of H_2 reference gas after H_3^+ correction was $<\pm 1$‰. Analytical accuracy and precision of TC/EA/IRMS system were determined using Polyethylene Foil (PEF1, National Institute of Standards and Technology (NIST)) ($\delta D_{vsmow} = -100.3$‰) standard. The root-mean-square error ($RMS = (\Sigma d^2/n)^{1/2}$, where $d = \delta D_{expected} - \delta D_{measured}$, n = number of measurements) was 1.3‰. Hydrogen isotopic compositions of kerogen samples are reported based on triplicate analyses. Standard deviations of kerogen δD values range between 0‰ and 1‰. δD values are reported relative to VSMOW based on a reference gas calibrated against PEF1 analyzed online.

2.4. Compound-specific δD analyses

Twenty-three samples from the adducted fraction and 7 samples from the non-adducted fraction were analyzed using a ThermoFinnigan Delta-Plus XP mass spectrometer connected to an Agilent 6890A gas chromatograph through the ThermoFinnigan GC/TC pyrolysis interface. Compound co-elution and the presence of unresolved complex mixture in the non-adducted fraction limited the number of samples available for isoprenoid measurements. The H_3-factor was determined similarly to the procedure described above. Reproducibility of H_2 reference gas δD values after H_3^+ correction was $<\pm 1$‰. Analytical accuracy and precision of the GC/TC/IRMS system were determined using two sets of external coinjected mixtures of organic D/H reference compounds: "nC_{16}–nC_{30} alkane" mixture and "5α-androstane, squalane, hentetracontane (nC_{41})" mixture; isotopic ratios measured off-line by A. Schimmelmann, Indiana University. RMS error for hydrogen isotopic measurements of these compounds was 5.1‰ ($n = 325$).

Hydrogen isotopic compositions of *n*-alkanes and isoprenoids from Gabon samples are reported based on duplicate

analyses of well-resolved peaks. Isodat NT Version 1.5 was used for data processing of *n*-alkane measurements. Because this version of Isodat does not account for large increases (up to 750 mV during analyses of non-adducted saturate fractions of the Gabon samples) in mass 2 background during H_3^+ correction, a modified version of Excel Visual Basic codes (specifically developed for this purpose by Alex Sessions et al. (2001)) was used to process data for the isoprenoid fractions. Standard deviations of *n*-alkane δD values range between 0‰ and 10‰; for the majority of compounds the values were <4‰. Standard deviations of pristane and phytane varied between 0‰ and 7‰. Hydrogen isotopic compositions of individual compounds are expressed relative to VSMOW based on coinjected internal standards (5α-androstane and hentetracontane).

3. Results

3.1. Biomarkers and vitrinite reflectance

Changes in OM maturity with depth are displayed graphically in Fig. 4. Both bulk and biomarker indicators show an increase in OM thermal maturity down the core from immature to early mature. Based upon the data from $22S/(22S+22R)$ C_{31} homohopanes (the value of 0.6 for this ratio is equivalent to $R_o = 0.6$; (Peters and Moldowan, 1993)), $20S/(20S+20R)$ C_{29} steranes ($0.4 \sim R_o = 0.6$), and $Ts/(Ts+Tm)$ ($0.5 \sim R_o = 0.6$) ratios, we estimate the onset of oil window at a depth interval between ~750 and 800 m. Somewhat greater levels of thermal maturity indicated by the vitrinite reflectance can be attributed to a lower sensitivity of this parameter (when compared to biomarkers) at this level of OM maturity (Peters and Moldowan, 1993).

3.2. Kerogen and compound-specific δD values

Fig. 5a shows the distribution of δD values of nC_{17} and nC_{29} alkanes, pristane, phytane, and kerogen plotted against depth in well ONEZ-1. Analysis of these data indicates a slight overall D-enrichment over depth and with increasing maturity in both nC_{17} and nC_{29} alkanes as well as approximately 5–10‰ decrease in the isotopic difference between these compounds ($\Delta D = \delta D\ nC_{17} - \delta D\ nC_{29}$). The δD values of kerogen samples generally fall within the range of the *n*-alkanes throughout the section. However, no close correspondence between isotopic patterns of kerogen and *n*-alkanes of either short or long-chain length is observed. Large variations in δD values (up to 40‰ for nC_{17}, up to 30‰ for nC_{29} and up to 10‰ for kerogen) among closely spaced samples are evident throughout the core and are preserved even at the bottom of the section. Standard deviations (σ) of a moving average of 5 points calculated for nC_{17} and nC_{29} fluctuate from 5‰ to 16‰ and from 2‰ to 12‰, respectively (Fig. 5b). σ maximum values correspond to the middle and bottommost parts of the section. σ values of kerogen range between 6‰ and 11‰, peaking between 500 and 600 m depth. δD values of isoprenoids behave very differently in comparison with those of *n*-alkanes and kerogen. Hydrogen isotopic ratios of pristane and phytane increase dramatically and approach those of nC_{17} in the samples closest to the oil window (Fig. 5c). Fig. 6 displays the distribution of δD values of *n*-alkanes of various chain lengths. A general pattern of increasing δD values with increasing *n*-alkane chain length characterizes all samples. The pattern is particularly evident below 600 m depth.

4. Discussion

4.1. Hydrogen isotopic exchange

Mechanisms for hydrogen isotopic exchange between lipids and formation water fall into two broad categories. In the first, reversible ionic hydrogen exchange is catalyzed by clays (Alexander et al., 1984). This process is favored in branched molecules that contain tertiary carbons, which induce hydrogen exchange at the adjacent secondary carbons. Isoprenoids like pristane and phytane have a large

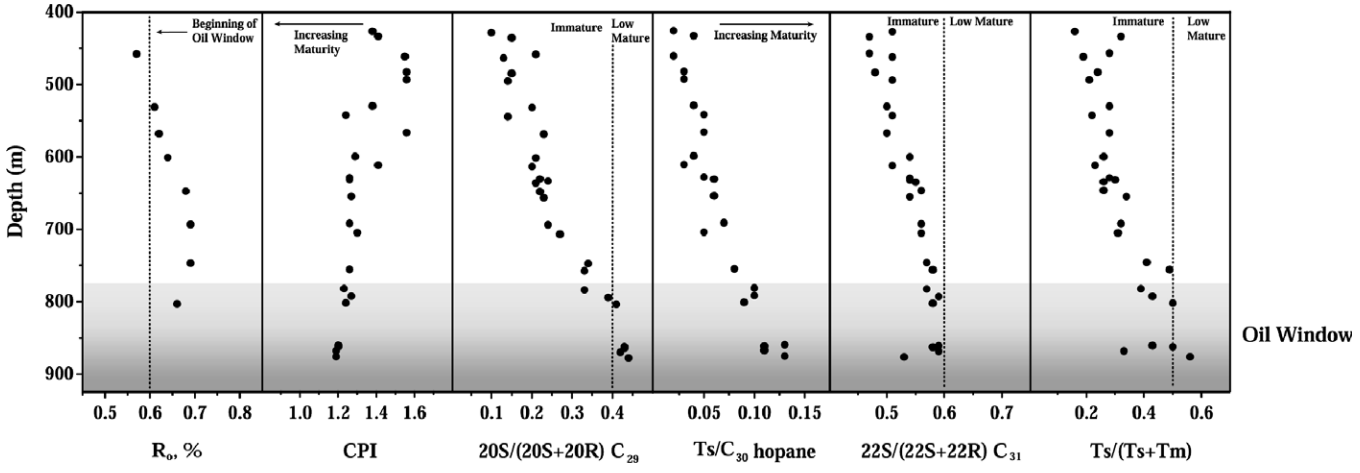

Fig. 4. Maturity bulk and biomarker parameters. Literature-based numerical values corresponding to the onset of oil window are shown using vertical dashed lines (see Section 3.1 for further discussion). The oil window in core ONEZ-1 is shown using the shaded area.

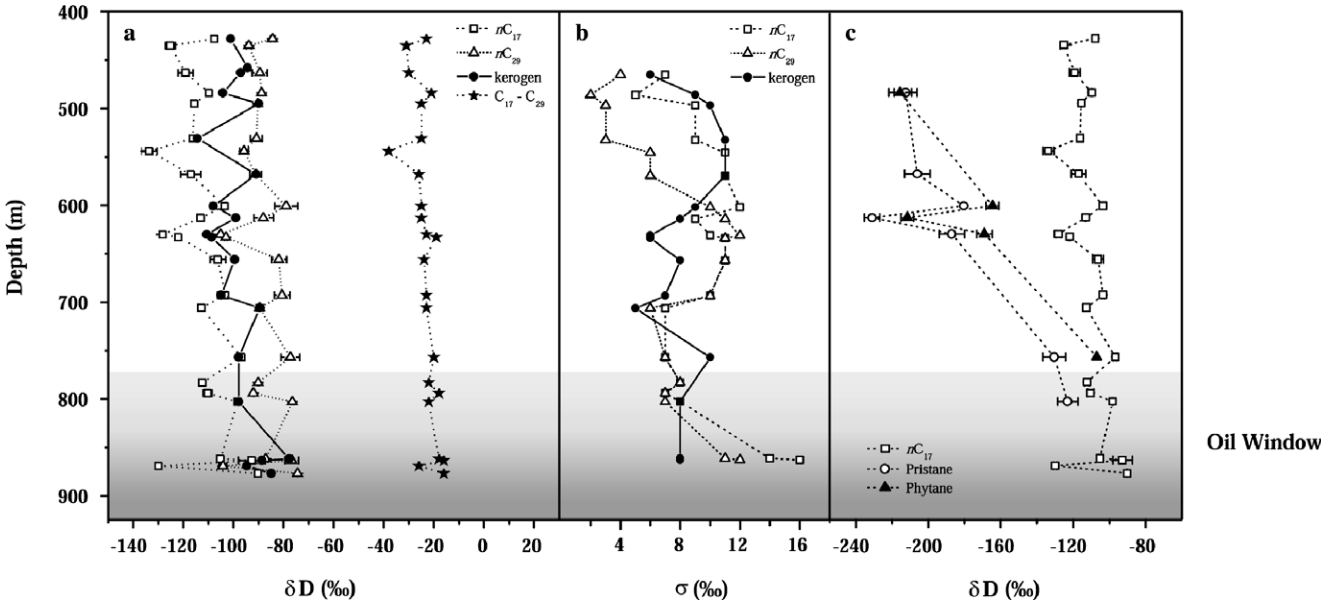

Fig. 5. (a) Hydrogen isotopic composition of nC$_{17}$ and nC$_{29}$ alkanes, kerogen, and $\Delta D_{nC17-nC29}$. (b) Standard deviations of a moving average of 5 points calculated for nC$_{17}$, nC$_{29}$, and kerogen. (c) Hydrogen isotopic composition of pristane, phytane, and nC$_{17}$.

number (18 and 20, respectively) of secondary carbons adjacent to tertiary carbon sites. If the hydrogen on such secondary sites exchanged with isotopically enriched formation waters, this would result in an extensive shift of δD values of these compounds.

The second category involves the irreversible isotopic transfer between OM and formation waters as a result of free-radical reactions during OM thermal maturation (Lewan, 1997). Free-radical sites are formed either by abstraction of hydrogen atoms through reactions with other free radicals or by thermal cracking. This process favors hydrogen transfer at tertiary and secondary carbons in comparison with primary carbons, because of a greater stability of radicals at the former sites.

Free-radical reactions are typically associated with elevated thermal conditions and significant molecular stereochemical and structural alteration. However, both maturation of OM and a prolonged contact with excess formation water in the presence of catalysts can yield hydrogen exchange reactions in sedimentary OM. Unlike the free radical processes, equilibrium exchange reactions do not require (at least theoretically, Sessions et al., 2004) high temperatures (>30 °C). Equilibrium fractionation factors are likely larger at lower temperatures, although experimental data are needed.

Recognizing the effects of equilibrium exchange in immature samples is difficult. Large contrasts between δD values of different types of compounds, the approach taken by Andersen et al. (2001), could arise from differences in water–lipid fractionation factors. Large fractionation factors at low temperatures may mimic the magnitude of biological fractionation of sedimentary lipids with ambient water (e.g., Yang and Huang (2003)). The problem of identifying the extent of isotopic exchange is compounded when OM is derived from multiple sources having similar biological δD values or when the isotopic composition of growth water does not vary significantly (e.g., compare arguments for a lack of extensive hydrogen exchange in Yang and Huang (2003) and Dawson et al. (2004)). An alternate approach is to compare calculated (for equilibrium) and observed δD values for different types of compounds. This approach, however, is limited by large uncertainties regarding equilibrium fractionation factors (Sessions et al., 2004).

Our hydrogen isotopic and thermal maturity data are considered in the context of hydrogen exchange processes in order to address the following questions. To what extent are D values of n-alkyl lipids from Gabon affected by post-depositional hydrogen equilibrium exchange? What is the influence of thermal maturity on δD values and can thermal maturity indicators be used to estimate the potential for isotopic alteration of preserved biomarker compounds?

4.2. Effects of equilibrium exchange on δD values

Sessions et al. (2004) surveyed previous literature and provided results of their own laboratory experiments concerning the factors that may influence equilibrium exchange reactions of carbon-bound hydrogen. Such factors (primarily OM type, temperature, and the presence of catalysts) control both equilibrium isotope fractionation and rates of hydrogen exchange. Data provided by Sessions et al. (2004) for these parameters are used here to calculate the isotopic composition of n-alkanes and isoprenoids in equilibrium with formation water. Calculation results are then compared with the empirical data from well ONEZ-1.

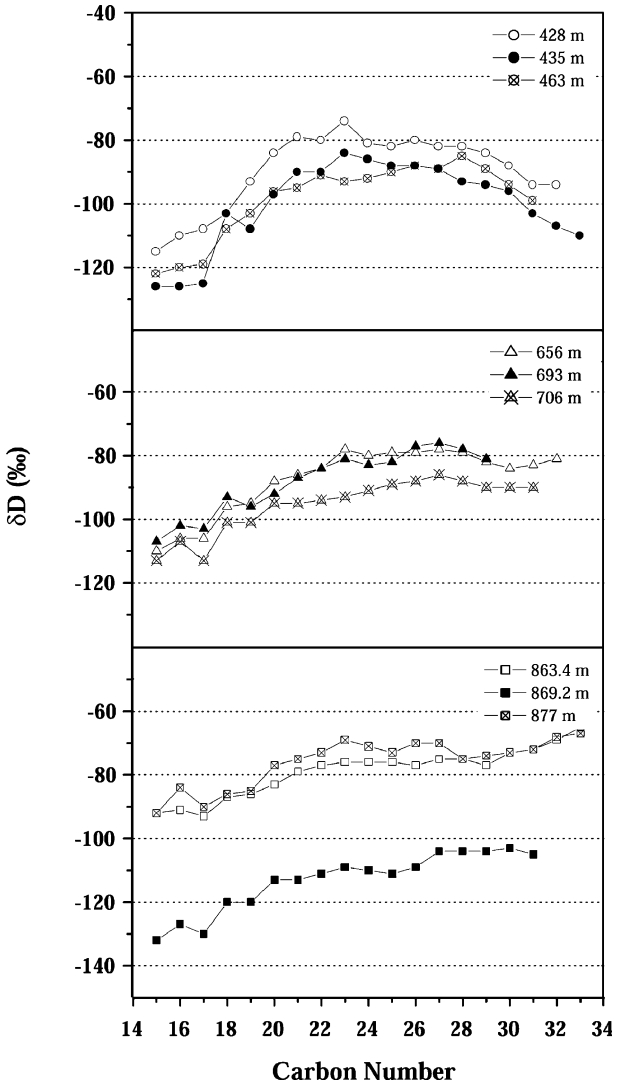

Fig. 6. Hydrogen isotopic composition of *n*-alkanes for nine representative samples from the upper, middle, and lower sections of the core.

We use theoretically calculated equilibrium fractionation factors (α) between lipid and water hydrogen for three different organic H positions (Sessions et al., 2004):

Primary H $(\mathbf{CH}_3-)$ $\alpha_{l/w} = 0.837$; $\sigma = 0.078$,

Secondary H $(-\mathbf{CH}_2-)$ $\alpha_{l/w} = 0.944$; $\sigma = 0.102$,

Tertiary H $(-\mathbf{CH})$ $\alpha_{l/w} = 0.812$; $\sigma = 0.080$,

to calculate the isotopic equilibrium composition of $n\mathrm{C}_{17}$ alkane, pristane, and phytane.

Two isotopic compositions of water were used (0‰ and −70‰, VSMOW) to cover a possible range of isotopic compositions of formation water originating from tropical rift lakes within the interior of Gondwana in Early Cretaceous. The results of these calculations are shown in Table 1. Experimental α values (at 35 °C; Thomson, 1960; Meloche et al., 1977), match theoretical (at 27 °C) values for the primary and secondary hydrogen atoms, although we caution that the α values used for calculations are not adequately constrained for thermal conditions typical of sedimentary basins. α values (Sessions et al., 2004) have uncertainties that are similar in magnitude to the calculated δD values of *n*-alkanes and isoprenoids (Table 1).

Isotopic differences in observed *n*-alkanes ($n\mathrm{C}_{17}$) and isoprenoids δD values (Fig. 5c) in the upper section of the well ONEZ-1 are larger than those calculated for equilibrium, (60–100‰ observed vs. ~40‰ at equilibrium). A drastic shift in δD values of both pristane and phytane deeper in the section could indicate α values are significantly reduced at depth and, in fact undergo a sudden drop over 150 m (with only <5 °C rise in temperature). However, it is more likely that *n*-alkanes and isoprenoids were out of equilibrium with formation water above ~750 m and that hydrogen exchange reactions are accelerated below this depth. In support of this interpretation, we note maturity biomarker parameters experienced more extensive stereochemical rearrangements below ~750 m (Fig. 4).

Our results confirm previous findings of a shift toward less negative δD values of isoprenoids in both thermally mature sedimentary OM and oils (Li et al., 2001; Dawson et al., 2004, 2005; Schimmelmann et al., 2004; Sessions et al., 2004). Large isotopic differences (in excess of 100‰) between *n*-alkyl and isoprenoid lipids reported for modern organisms (Sessions et al., 1999, 2002; Chikaraishi et al., 2004; Chikaraishi and Naraoka, 2005), and which appear to have been preserved in the upper section of the core in this study, were rapidly diminished due to a more extensive D-enrichment of isoprenoids in comparison with *n*-alkyl lipids.

4.3. Effects of thermal maturation on δD values

We find an overall slight D-enrichment of *n*-alkanes with depth over the interval corresponding to significant stereochemical changes associated with thermal maturation (Fig. 5a). Because of absence of a similar shift in oxygen isotopic composition of lacustrine carbonates from the

Table 1
Calculated δD values (‰, VSMOW) of pristane, phytane, and $n\mathrm{C}_{17}$ alkane at equilibrium with formation water

	Number of primary H atoms	Number of secondary H atoms	Number of tertiary H atoms	δD of water 0‰	δD of water −70‰
Resultant molecular isotopic compositions					
Pristane	18	18	4	−117 (±89)	−179 (±83)
Phytane	18	20	4	−114 (±90)	−177 (±84)
$n\mathrm{C}_{17}$ alkane	6	30	0	−74 (±98)	−139 (±92)

Two different isotopic compositions of hypothetical formation water were used for calculations.

well ONEZ-1 (Pedentchouk, 2004), we rule out a paleoenvironmentally driven long term shift in δD values of source water. Likewise, it is unlikely that δD values of formation waters differ drastically within just several meters in the well ONEZ-1, as suggested by the observations of Schimmelmann et al. (2004). Persistent and large differences between δD values of *n*-alkanes and large variations in δD values among closely spaced samples throughout the core (Fig. 5b), suggest against extensive alteration of biological δD values of *n*-alkanes by free radical processes which would homogenize molecular δD values (Hoering, 1977). However, we suggest the *n*-alkane isotopic shifts represent a slight post-depositional alteration of primary δD signal and progressive D-enrichment of longer chain *n*-alkanes with increasing maturity down the core (Fig. 6). An extensive review of the factors that may cause this phenomenon was provided by Schimmelmann et al. (2004), who argued that kinetic isotope effects accompanying hydrocarbon generation from kerogen may provide the most viable explanation. Progressive decrease of CPI values (Fig. 4) over depth in the well ONEZ-1 supports this explanation. Newly formed *n*-alkanes may have acquired characteristic D-depletion/D-enrichment pattern and started to gradually dilute the primary biological derived δD signature.

Hydrogen isotopic composition of pristane and phytane increase dramatically and approach those of *n*-alkanes in the samples closest to the oil window. We speculate that free radical processes were not a major factor in the observed changes because these compounds have significantly fewer secondary and a greater proportion of primary carbons in comparison with *n*-alkanes (Table 1). Currently information regarding the kinetics of free radical H-transfer processes suggests exchange at tertiary sites is favored; however, mass balance calculations indicate that having 4 tertiary carbons would be insufficient to account for the large shift in δD values observed in Fig. 5c. Thus, free-radical hydrogen transfer could actually affect pristane and phytane less than *n*-alkanes. Therefore, we propose that significant changes in δD values of isoprenoids were caused mainly by enhanced equilibrium exchange reactions which favor the more abundant secondary sites adjacent to the tertiary centers.

The overlapping of δD values of kerogens and *n*-alkanes even at the top of the section is surprising, because kerogen is typically D-enriched in comparison with saturated hydrocarbons at low levels of OM maturity (Schoell, 1984; Schou et al., 1985). Kerogen preferential D-enrichment is anticipated due to its overall higher susceptibility to H-transfer in comparison with saturated hydrocarbons (Schimmelmann et al., 1999). This pattern of δD values suggests that thermal maturation had a similar effect on hydrogen isotopic composition of both kerogens and *n*-alkanes. The fact that the pattern of kerogen δD values over depth does not correspond to that of individual *n*-alkane values may indicate differences in the proportion of material contributed to the kerogen by *n*-alkanes of different chain length and perhaps contribution from other OM fractions.

5. Conclusion

Hydrogen isotopic measurements complemented by bulk and molecular maturity parameters were conducted on a continuous 450 m core from the Lower Cretaceous lacustrine Kissenda Fm., in the Gabon Basin. This study provides the most continuous uninterrupted record of δD value of *n*-alkanes, isoprenoids, and kerogen through the transition from thermally immature to early mature OM. Integration of high resolution analytical data and computational results indicates the following:

1. Large hydrogen isotopic differences (up to 100‰) between *n*-alkanes and isoprenoids (the pattern typical of modern biomass) are maintained in the upper section of the core, indicating that both compound classes have the potential to preserve the original biological isotopic signal in ancient sediments before the beginning stages of oil generation and in the absence of extensive hydrogen exchange reactions.
2. Physico-chemical processes that resulted in OM maturation in the deeper section of the early mature part of the core did not significantly affect the hydrogen isotopic composition of either *n*-alkanes or kerogen. However, δD values of isoprenoids (pristane and phytane) were affected greatly (D-enrichment up to 90‰) at depth corresponding to the beginning of the oil window.
3. Extensive alteration of the primary biologically derived δD signal in isoprenoids could be attributed to the presence of tertiary carbon atoms in their structure, resulting in greater hydrogen isotopic transfer during equilibrium exchange reactions after sedimentary burial. A minor alteration of δD values of *n*-alkanes exhibited by a slight overall shift toward D-enrichment over depth and by a characteristic D-enrichment of long-chain homologues could have resulted from addition of newly formed *n*-alkanes during bitumen generation at higher thermal maturity.

This study demonstrates that future applications of hydrogen isotopes in geological samples are more likely to benefit from analysis of *n*-alkanes in comparison with isoprenoid compounds. Greater resistance of *n*-alkanes to hydrogen isotope exchange/transfer over geologic time (particularly in organic rich rocks with low permeability) combined with a comparatively easy methodology for isolation and purification make *n*-alkanes an ideal target for compound-specific work. However, greater susceptibility of isoprenoid compounds to hydrogen transfer should not be regarded as a disadvantage. Extensive isotopic shifts observed in this continuous record provide further evidence that δD values of isoprenoids may serve as a useful tool for determining the state of OM maturity in sedimentary basins.

Acknowledgments

We thank members of the Penn State Congo Basin consortium, which include Anadarko, Arco, Chevron, Conoco, the Japan National Oil Corporation, Mobil, Norsk Hydro, Phillips and Texaco, for financial support of this project. We are grateful to Conoco for providing samples from well ONEZ-1 in Gabon. Arndt Schimmelmann and Peter Sauer contributed tremendously with their analytical and methodological input. Dennis Walizer, Pratigya Pollisar, Teresa Diel, and Chris Lernihan provided technical and laboratory assistance. We thank Gareth Mitchell for vitrinite reflectance analyses. We are grateful to Stephen Meyers for his assistance with statistical treatment of δD data. This research was supported by an ACS PRF research grant to K.H. Freeman as well as the BP Fellowship and the AAPG Grant-in-Aid to N. Pedentchouk. Alex Sessions, Arndt Schimmelmann, and one anonymous reviewer provided very constructive reviews which greatly improved the manuscript.

Associate editor: Roger Summons

References

Alexander, R., Kagi, R.I., Larcher, A.V., 1984. Clay catalysis of alkyl hydrogen exchange reactions—reaction mechanisms. *Org. Geochem.* **6**, 755–760.

Andersen, N., Paul, H.A., Bernasconi, S.M., McKenzie, J.A., Behrens, A., Schaeffer, P., Albrecht, P., 2001. Large and rapid climate variability during the Messinian salinity crisis: evidence from deuterium concentrations of individual biomarkers. *Geology* **29**, 799–802.

Bray, E.E., Evans, E.D., 1961. Distribution of *n*-paraffins as a clue to recognition of source rocks. *Geochim. Cosmochim. Acta* **22**, 2–15.

Burgoyne, T.W., Hayes, J.M., 1998. Quantitative production of H_2 by pyrolysis of gas chromatographic effluents. *Anal. Chem.* **70**, 5136–5141.

Chikaraishi, Y., Naraoka, H., 2003. Compound-specific δD–$\delta^{13}C$ analyses of *n*-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* **63**, 361–371.

Chikaraishi, Y., Naraoka, H., 2005. $\delta^{13}C$ and δD identification of sources of lipid biomarkers in sediments of Lake Haruna (Japan). *Geochim. Cosmochim. Acta* **69**, 3285–3297.

Chikaraishi, Y., Matsumoto, K., Ogawa, N.O., Suga, H., Kitazato, H., Ohkouchi, N., 2005. Hydrogen, carbon and nitrogen isotopic fractionations during chlorophyll biosynthesis in C3 higher plants. *Phytochemistry* **66**, 911–920.

Chikaraishi, Y., Naraoka, H., Poulson, S.R., 2004. Carbon and hydrogen isotopic fractionation during lipid biosynthesis in a higher plant (*Cryptomeria japonica*). *Phytochemistry* **65**, 323–330.

Davison, I., 1999. Tectonics and hydrocarbon distribution along the Brazilian South Atlantic margin. In: Cameron, N.R., Bate, R.H., Clure, V.S. (Eds.), *Oil and Gas Habitats of the South Atlantic*. The Geological Society, London, pp. 133–151.

Dawson, D., Grice, K., Alexander, R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). *Org. Geochem.* **36**, 95–104.

Dawson, D., Grice, K., Wang, S.X., Alexander, R., Radke, J., 2004. Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions. *Org. Geochem.* **35**, 189–197.

Hilkert, A.W., Douthitt, C.B., Schlüter, H.J., Brand, W.A., 1999. Isotope ratio monitoring gas chromatography/mass spectrometry of D/H by high temperature conversion isotope ratio mass spectrometry. *Rapid Commun. Mass Spectrom.* **13**, 1226–1230.

Hoering, T.C., 1977. The stable isotopes of hydrogen in Precambrian organic matter. In: Ponnamperuma, C. (Ed.), *Chemical Evolution of the Early Precambrian*. Academic Press, New York, pp. 81–86.

Huang, Y., Shuman, B., Wang, Y., Thompson, W.I., 2002. Hydrogen isotope ratios of palmitic acid in lacustrine sediments record late Quaternary climate variations. *Geology* **30**, 1103–1106.

Lewan, M.D., 1997. Experiments on the role of water in petroleum formation. *Geochim. Cosmochim. Acta* **61**, 3691–3723.

Li, M., Huang, Y., Obermajer, M., Jiang, C., Snowdon, L.R., Fowler, M.G., 2001. Hydrogen isotopic compositions of individual alkanes as a new approach to petroleum correlation: case studies from the Western Canada Sedimentary Basin. *Org. Geochem.* **32**, 1387–1399.

Liu, W., Huang, Y., 2005. Compound specific D/H ratios and molecular distributions of higher plant leaf waxes as novel paleoenvironmental indicators in the Chinese Loess Plateau. *Org. Geochem.* **36**, 851–860.

Meloche, H.P., Monti, C.T., Cleland, W.W., 1977. Magnitude of the equilibrium isotope effect on carbon–tritium bond synthesis. *Biochim. Biophys. Acta* **480**, 517–519.

Pedentchouk, N., 2004. Lacustrine paleoenvironments from stable isotopes of hydrogen and carbon in lipids. Ph.D. Dissertation, Pennsylvania State University, State College, Pennsylvania, USA.

Peters, K.E., Moldowan, J.M., 1993. *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice Hall, Englewood Cliffs.

Radke, J., Gleixner, G., 2003. Compound-specific hydrogen isotopes of biomarkers as paleoclimatic, paleoenvironmental and biosynthetic proxy in Late Paleozoic sediments. In: *2003 GSA Annual Meeting, Abstracts with Programs*. Geological Society of America, p. 484.

Robl, T.L., Davis, B.H., 1993. Comparison of the HF–HCl and HF–BF_3 maceration techniques and the chemistry of resultant organic concentrates. *Org. Geochem.* **20**, 249–255.

Sachse, D., Radke, J., Gleixner, G., 2004. Hydrogen isotope ratios of recent lacustrine sedimentary *n*-alkanes record modern climate variability. *Geochim. Cosmochim. Acta* **68**, 4877–4889.

Sauer, P.E., Eglinton, T.I., Hayes, J.M., Schimmelmann, A., Sessions, A.L., 2001. Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions. *Geochim. Cosmochim. Acta* **65**, 213–222.

Schefuß, E., Schouten, S., Schneider, R.R., 2005. Climatic controls on central African hydrology during the past 20,000 years. *Nature* **437**, 1003–1006.

Schimmelmann, A., Lewan, M.D., Wintsch, R.P., 1999. D/H isotope ratios of kerogen, bitumen, oil, and water in hydrous pyrolysis of source rocks containing kerogen types I, II, IIS, and III. *Geochim. Cosmochim. Acta* **63**, 3751–3766.

Schimmelmann, A., Sessions, A., Boreham, C.J., Edwards, D.S., Logan, G.A., Summons, R.E., 2004. D/H ratios in terrestrially sourced petroleum systems. *Org. Geochem.* **35**, 1169–1195.

Schoell, M., 1984. Wasserstoff- und Kohlenstoffisotope in organischen Substanzen, Erdölen und Erdgasen. *Geologisches Jahrbuch, Reihe D* **D67**, 3–161, Schweizerbarth, Stuttgart (in German).

Schou, L., Eggen, S., Schoell, M., 1985. Oil–oil and oil–source rock correlation, Northern North Sea. In: Thomas, B.M. (Ed.), *Petroleum Geochemistry in Exploration of the Norwegian Shelf*. Graham and Trotman, London, pp. 101–117.

Sessions, A.L., Burgoyne, T.W., Hayes, J.M., 2001. Correction of H_3^+ contribution in hydrogen isotope ratio monitoring mass spectrometry. *Anal. Chem.* **73**, 192–199.

Sessions, A.L., Burgoyne, T.W., Schimmelmann, A., Hayes, J.M., 1999. Fractionation of hydrogen isotopes in lipid biosynthesis. *Org. Geochem.* **30**, 1193–1200.

Sessions, A.L., Jahnke, L.L., Schimmelmann, A., Hayes, J.M., 2002. Hydrogen isotope fractionation in lipids of the methane-oxidizing

bacterium *Methylococcus capsulatus*. *Geochim. Cosmochim. Acta* **66**, 3955–3969.

Sessions, A.L., Sylva, S., Summons, R.E., Hayes, J.M., 2004. Isotopic exchange of carbon-bound hydrogen over geologic timescales. *Geochim. Cosmochim. Acta* **68**, 1545–1559.

Smith, F.A., Freeman, K.H., in press. Influence of physiology and climate on δD of leaf wax *n*-alkanes from C_3 and C_4 grasses. *Geochim. Cosmochim. Acta*.

Teisserenc, P., Villemin, J., 1990. Sedimentary basin of Gabon; geology and oil systems. In: Edwards, J.D., Santogrossi, P.A. (Eds.), *Divergent/Passive Margin Basins*. American Association of Petroleum Geologists, Tulsa, Oklahoma, pp. 117–199.

Thomson, J.F., 1960. Fumarase activity in D_2O. *Arch. Biochem. Biophys.* **90**, 1–6.

Wakeham, S.G., Pease, T.K., 1992. *Lipid Analysis in Marine Particle and Sediment Samples. A Laboratory Handbook*. Savannah, Georgia.

Xie, S., Nott, C.J., Avsejs, L.A., Volders, F., Maddy, D., Chambers, F.M., Gledhill, A., Carter, J.F., Evershed, R.P., 2000. Palaeoclimate records in compound-specific δD values of a lipid biomarker in ombrotrophic peat. *Org. Geochem.* **31**, 1053–1057.

Yang, H., Huang, Y., 2003. Preservation of lipid hydrogen isotope ratios in Miocene lacustrine sediments and plant fossils at Clarkia, northern Idaho, USA. *Org. Geochem.* **34**, 413–423.